ELECTRODE POTENTIAL OF NICKEL. PART III. MECHANISM OF THE RE-ACTIVATION OF THE PASSIVE STATE OF NICKEL.

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In the former papers[1] only the experimental parts of the measurement of the electrode potential were described, while in the present paper the foregoing results are discussed from a thermodynamical standpoint and further the mechanism underlying the re-activation of the passive state of nickel is explained.

(I) **Catalytic Action of Nickel.** In Parts I and II, it has been shown that, if we exclude all traces of air or oxygen from the cell, the nickel gives a constant and reversible potential of active nickel in an atmosphere of hydrogen, and also of nitrogen; and that, if however the nickel used is one which has been affected by previous exposure to the air, the introduction of hydrogen causes rapid re-activation. The passive state of nickel, therefore, is extremely sensitive to hydrogen, and it is highly probable that the re-activation by hydrogen is a simple reduction of the surface of the superficially oxidized electrode. On the other hand, it has been definitely ascertained that nickel catalyses the combination of hydrogen and oxygen, an action which has a close relation to the above facts. Pease and Taylor[2] have suggested that nickel will catalyse this reduction of the oxide even at room temperature. The work of Larson and Smith[3] on the measurement of the synthesis of water in the presence of a nickel catalyst has shown that in the case of gas mixtures containing as much as 2% of oxygen the combination of hydrogen and oxygen occurs in contact with metallic nickel—even at low temperatures which are not far from room temperature—and this combination is fairly measurable at 34°C., though at these low temperatures a superficial oxidation of nickel readily takes place. They have also shown that the resulting nickel oxide is completely reduced at 34°C. in the presence of pure hydrogen. The same experimental results were repeated qualitatively by Benton and Emmett.[4] According to the view of the two latter investigators, the

(1) This journal, **3** (1928), 57 and 253.
(2) *J. Am. Chem. Soc.*, **44** (1922), 1644.
(3) *J. Am. Chem. Soc.*, **47** (1925), 346.
(4) *J. Am. Chem. Soc.*, **48** (1926), 632.

catalytic combination proceeds by a mechanism of successive oxidation and reduction, as found by Pease and Taylor[1] in their experiments on metallic copper. By the measurement of the rate of reduction of nickel oxide they have found that the reduction of this oxide by hydrogen is an interfacial reaction, proceeding at the interface between nickel oxide and nickel, that is, that there is a reaction the rate of which depends on the extent of the area and on the nature of the contact between the two solid phases. Consequently, starting with pure nickel oxide the initial rate is practically zero, but after a certain lapse of time, which is longer at lower temperatures, reduction begins and is accelerated autocatalytically.

In view of these facts, it is reasonable to consider that the cause of the sudden change in nickel caused by the action of hydrogen from the passive state to the more active upon the introduction of hydrogen into the cell,—as found in cell No. 7′ of the present writer's experiment or in the cell of Schoch[2], the electrodes of which had been so affected by previous exposure to the air,—is mainly the catalytic reduction of the superficially oxidized surface of the nickel electrode.

The same catalytic action should have prevailed also in cells Nos. 6 and 7. However, for the fuller explanation of the results in the case of these cells, a theoretical calculation of the equilibrium conditions in the nickel half-cells is necessary, and this will be given in the next section.

(II) **Nickel-Hydrogen Equilibrium in Aqueous Nickel Salt Solution.** In the nickel half-cell, there should be established an equilibrium between the electrode nickel and the hydrogen ion resulting from the hydrolysis of nickel salt, and the reactions involved will be expressed by the following equations : —

$$Ni + 2H^+ = Ni^{++} + H_2 \quad \ldots\ldots\ldots\ldots (1)$$

$$Ni^{++} + 2H_2O = Ni(OH)_2 + 2H^+ \quad \ldots\ldots\ldots\ldots (2)$$

Combining these two with the equation for the dissociation of nickel hydroxide,

$$Ni(OH)_2 = Ni^{++} + 2OH^- \quad \ldots\ldots\ldots\ldots (3)$$

we have

$$Ni + 2H_2O = Ni^{++} + 2OH^- + H_2 \quad \ldots\ldots\ldots\ldots (4)$$

Let K_1, K_2, K_3, K_4 be the corresponding equilibrium constant of the reactions, respectively. Then, we have the relation,

$$K_4 = K_1 \times K_2 \times K_3 = K_1 \times K_w^2 = p_{H_2} \times a_{Ni^{++}} \times a_{OH^-}^2 \ldots\ldots\ldots\ldots (5),$$

(1) Loc. cit.

(2) *Am. Chem. J.*, **41** (1909), 208.

where K_w is the dissociation constant of water. Therefore K_4 is obtainable, if K_1 is known.

Reaction (1) takes place in the cell,

$$H_2\,(p)\ |\ H^+\ (a_{H^+})\ \|\ Ni^{++}\ (a_{Ni^{++}})\ |\ Ni$$

The free energy decrease $(-\Delta F)$ accompanying the change in state in this cell, and corresponding to the passage of two faradays, may be expressed by the following thermodynamic expression,

$$-\Delta F = 2FE_0 - RT \ln \frac{a_{Ni^{++}} \cdot p_{H_2}}{a^2_{OH^-}}$$

where E_0 is the normal electrode potential of nickel. The value of E_0 is -0.2496 volt at 25°C. according to the present writer's measurement. Therefore,

$$-\Delta F_{298} = 11518 - 1365 \log \frac{a_{Ni^{++}} \cdot p_{H_2}}{a^2_{H^+}}$$

At equilibrium, that is when $-\Delta F = 0$, we obtain

$$K_1 = \frac{a_{Ni^{++}} \times p_{H_2}}{a^2_{H^+}} = 10^{8.4387} \quad \ldots\ldots\ldots\ldots (6)$$

Taking $K_w = 1.005 \times 10^{-14}$ at 25°C.[1] from (5), we find that

$$K_4 = K_1 \times K_w^2 = 10^{-19.557}$$

$$p_{H_2} \times a_{Ni^{++}} \times a^2_{OH^-} = 10^{-19.557} \quad \ldots\ldots\ldots\ldots (7)$$

In this system the value of the product $[a_{Ni^{++}} \times a^2_{OH^-}]_0$ at equilibrium varies inversely with the variation of the partial pressure of the hydrogen, p_{H_2}. If the system is subjected to a definite pressure of hydrogen, the activity product $[a_{Ni^{++}} \times a^2_{OH^-}]_0$ will be fixed. Then when the partial pressure of the hydrogen is equal, for instance, to one atmosphere, equilibrium is attained at the point where the activity product $[a_{Ni^{++}} \times a^2_{OH^-}]$ equals $10^{-19.557}$. In an actual case, however, equilibrium can be established only when the value of the activity product $[a_{Ni^{++}} \times a^2_{OH^-}]_0$ in the solution at the equilibrium is less than or equal to that of the solubility product of $Ni(OH)_2$. But, if the amount of this product $[a_{Ni^{++}} \times a^2_{OH^-}]_0$ be greater than that of the solubility product, the true equilibrium, being disturbed by the precipitation of nickel hydroxide, will not result.

Only a small amount of the work connected with the solubility product of $Ni(OH)_2$ has been published and Britton's data[2] are the only ones which

(1) Lewis and Randall, "Thermodynamics."
(2) *J. Chem. Soc.*, **127** (1925), 2118.

were obtained by direct measurement. By an electromotive force method he measured the H^+ concentration in the solution of nickel chloride with a sufficient amount of NaOH solution added to induce the precipitation of $Ni(OH)_2$. It is, however, doubtful whether this method gives the actual value of a_{H^+}, because the precipitate of nickel hydroxide in contact with the platinized-platinum should be continuously reduced by hydrogen, and the nickel thus produced would disturb its action as a reversible hydrogen electrode.

Therefore, the solubility product may be calculated indirectly by combining the hydrolysis constant of nickel sulphate and the solubility of nickel hydroxide in water.

Inserting Denham's value[1] of hydrolysis constant in equation (5), $K_2 = 1.1 \times 10^{-13}$ or $10^{-12.96}$, a value which is somewhat uncertain but the only one existing, we obtain the value of the ionization constant of nicke hydroxide,

$$K_3 = \frac{a_{Ni} \times a^2_{OH^-}}{a_{Ni(OH)_2}} = \frac{K_w^2}{K_2}$$
$$= \frac{(1.005 \times 10^{-14})^2}{1.1 \times 10^{-13}} = 10^{-15.04} \quad . \quad . \quad . \quad . \quad (8)$$

By the combination of this ionization constant with the solubility of nickel hydroxide in water,[2] 1.27 mg./L. or 1.37×10^{-4} M/L., the molal concentration of nickel ion in the saturated aqueous solution of nickel hydroxide is found to be 3.16×10^{-7} or $10^{-6.50}$, from which, we have the solubility product,

$$[a_{Ni^{++}} \times a^2_{OH^-}]_{s.p.} = 1.256 \times 10^{-19} \text{ or } 10^{-18.901} \quad . \quad . \quad . \quad (9)$$

Solving equation (7) with this value of the solubility product, we have the corresponding partial pressure ${}_0p_{H_2}$,

$$\log {}_0p_{H_2} = -19.557 - 18.90094 = -0.657 \text{ or } \bar{1}.343$$
$${}_0p_{H_2} = 0.22 \text{ atm.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This is the critical pressure, above which only equilibrium conditions can be attained and if the partial pressure of hydrogen is less than this value, the nickel will tend to go into solution accompanied by the precipitation of $Ni(OH)_2$ until p_{H_2} rises to the critical value. Hence, if p_{H_2} be greater than ${}_0p_{H_2}$, equilibrium will be always set up, but if the p_{H_2} be less than ${}_0p_{H_2}$, true equilibrium can never be attained and the nickel should continue to be attacked.

(1) *J. Chem. Soc.*, **93** (1908), 60.
(2) Almkvist, *Z. anorg. allg. Chem.*, **103** (1918), 240.

(III) Discussion of the Results. Now, the experimental results obtained in the former papers will be discussed in the light of the preceding theoretical considerations.

In the first place, the case of cell No. 1 will be considered, where a solution of 0.05 M. $NiSO_4$ (containing $a_{Ni^{++}} = 0.05 \times 0.24$) was in contact with the reduced nickel under one atmospheric pressure of hydrogen, and the pressure required for the system to be in equilibrium will be calculated. The hydrogen ion concentration in 0.05 M. $NiSO_4$ at 25°C. is found to be 3.95×10^{-5} or $10^{-4.40}$ by the graphic interpolation from Denham's values, though they are of less order of accuracy. Then, from equation (6),

$$p_{H_2} = \frac{K_1 \times a^2_{H^+}}{a_{Ni^{++}}} = \frac{10^{8.44} \times 10^{2\times(-4.40)}}{0.05 \times 0.24} = 35.7 \text{ atms.}$$

The above calculation indicates that the nickel electrode is theoretically less noble than hydrogen under the conditions of the experiment and it should tend to go into solution with the evolution of the hydrogen on the nickel under one atmospheric pressure of hydrogen; the driving force for the corroding reaction is however

$$E_{H_2} = \frac{RT}{2F} \ln p_{H_2} = 0.02958 \log 35.7 = 0.0459 \text{ volt at } 25°C.$$

It is owing to this relatively small difference in the potential that the evolution of hydrogen is invisible, because the hydrogen overvoltage of nickel is usually high enough to offset the potential difference and prevent the gas evolution in bubbles. According to Thiel and Hammerschmidt,[1] the hydrogen overvoltage of nickel is 0.1375 volt.

On the other hand, in an atmosphere of nitrogen, as in cell No. 6 and No. 7, the nickel should go into the solution and form hydrogen until the solubilily product of nickel hydroxide is attained; the oxidized surface of the passive nickel electrode will be reduced by the catalysis of nickel or destroyed, so that the nickel becomes gradually active. But, at the moment when the solubility product of nickelous hydroxide is reached, the value p_{H_2} in the electrode should be equal to ${}_0p_{H_2}$ and no further solution of nickel can, therefore, take place. These are the reasons why the electromotive force of cells Nos. 6 and 7 rose gradually in the first, and then remained nearly constant at their own maximum values, i. e. above 0.6345 volt and 0.6355 volt, respectively, these values being a little below that of the active nickel in cell No. 1.

(IV) Results of Previous Workers. Now, with the above deduction, it seems possible to explain fairly the abnormal passive phenomena observed

(1) *Z. anorg. allg. Chem.*, **132** (1924), 15.

by previous workers in the measurements of the electrode potential of nickel.

In the first place, it is a remarkable fact that the potential of the nickel electrode is changed to an extraordinary degree on being treated with a solution of alkali hydroxide. The reversible potential of the reduced nickel in 1 N. $NiSO_4$ calculated from the writer's observed value is -0.276 volt, while in the case of the cathodic polarization of the electrode in an alkali solution a much less noble potential, i. e. as much as -0.33 volt, was found by Schweitzer[1]; the latter potential, however, gradually changed appreciably. Another interesting experiment giving a very low potential, -0.597 volt was made by Muthmann and Fraunberger.[2] The nickel having this low potential was prepared by electrolytic deposition on plaiunum from a neutral sulphate solution under a certain condition (at room temperature with 8 volts), and by the cathodic polarization of it with hydrogen in distilled water. Their experiment was however examined later by Thompson and Sage[3] who found that the high potential observed by the former investigators was that of a green deposit of a basic salt and not one of pure nickel.

In this connection, it may be supposed as the most possible case that a thin muddy coating of some basic salt or a film of colloidal hydroxide precipitate is formed on the electrode by the previous treatment and that this coating or film is catalytically reduced by hydrogen into nickel in a very fine state. Since the lower the electrode potential, the finer the metal powder, it is natural that the extremely fine nickel powder should give such abnormaly low potentials as those above mentioned at the moment, but that as this powder would tend to change to a more stable form with time the potential would gradually become normal.

If this is the case, then it is also possible that a similar abnormality may occur when the electrode is polarized even in an acid solution with hydrogen cathodically, so long as it has a chance of producing some basic salt or hydroxide on the very surface of the activated metal. This may possibly be the case when the activated surface, after being washed, has been wetted with water which might or might not contain the trace of acid, and was acted by the air while it was being transferred into the cell, as was done by Schoch.[4]

It will be remembered in this connection that pure iron quenched from an atmosphere of pure nitrogen gave a similar abnormality in its electromo-

(1) *Z. Elektrochem.*, **15** (1909), 607.
(2) *Sitz. Bayer. Akad. Wiss.*, **34** (1904), 201.
(3) *J. Am. Chem. Soc.*, **30** (1908), 714.
(4) Loc. cit.

tive force, as shown by the experiment of Richards and Behr.[1] This matter will be discussed in a paper which will be presented in the near future.

(V) **Free Energy.** The calculation of some important thermodynamic quantities relating to this subject have been made by combining the results obtained above with the existing data.

The Free Energy of the Formation of Nickel Hydroxide. Taking the solubility product of $Ni(OH)_2$ as $10^{-18.90}$ the free energy change for the equation

$$Ni(OH)_2 = Ni^{++}_{(1\ mol)} + 2OH^-_{(1\ mol)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

may be calculated

$$\Delta F_{298} = -RT \ln a_{Ni^{++}} \cdot a^2_{OH^-} = -1365 \times -18.90 = 25800 \text{ calories.}$$

Then, the free energy of formation of $Ni(OH)_2$ may be calculated as follows: —

From the first paper

$$Ni_{(s)} = Ni^{++} + 2\ominus; \qquad \Delta F_{298} = -11518 \text{ calories.}$$

and, according to Lewis and Randall ("Thermodynamics"),

$$\frac{1}{2} O_2 + \frac{1}{2} H_2 + \ominus = OH^-; \quad \Delta F_{298} = -37455 \text{ calories:}$$

hence

$$Ni_{(s)} + O_2 + H_2 = Ni^{++} + 2OH^-; \quad \Delta F_{298} = -86428 \text{ calories.}$$

Combining this value with that of (11) determined above, we have for the standard free energy of formation of $Ni(OH)_{2(s)}$,

$$Ni_{(s)} + O_2 + H_2 = Ni(OH)_{2(s)};$$
$$\Delta F_{298} = -112228 \text{ calories.}^* \quad . \quad . \quad . \quad . \quad (12)$$

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(1) *Z. physik. Chem.*, **58** (1907), 301.

* The value obtained from the solubility product used in the present paper is in good agreement with that obtained from the heat of formation of $Ni(OH)_2$ using the Nernst heat theorem, the entropy of the elements (Lewis and Randall, "Thermodynamics" p. 464) at 25°C. and the formula proposed by Latimer (*J. Am. Chem. Soc.*, **43** (1921), 818) for the entropy of solid salt. The heat of formation of $Ni(OH)_2$ in the reaction,

$$Ni_{(s)} + \frac{1}{2} O_2 + H_2O_{(l)} = Ni(OH)_{2(s)}$$

is 60840 cals. according to Thomsen (Landalt-Börnstein, "Physikalisch-Chemische Tabellen"), and that of the reaction

$$H_2 + \frac{1}{2} O_2 = H_2O_{(l)}$$

at 25°C. is 68270 cals. according to Lewis (*J. Am. Chem. Soc.*, **28** (1906), 1390), hence for

$Ni_{(s)} + O_2 + H_2 = Ni(OH)_{2(s)}$; $\Delta H = -60840 - 68270 = -129110$ cals.

$\Delta S = S_{Ni(OH)_2} - S_{Ni} - S_{O_2} - S_{H_2} = -56.5$ entropy unit at 298°K.

$\Delta F = \Delta H - T\Delta S = -129110 - (298 \times -56.5) = -112270$ cals.

The Free Energy Change in the Reduction of Nickel Oxide or Nickel Hydroxide. The free energy change in the reaction,

$$Ni(OH)_{2(s)} + H_{2(p\ atm.)} = Ni_{(s)} + 2H_2O_{(l)} \quad \ldots\ldots (13)$$

may be obtained from (12) by combination with the free energy of the formation of water. According to Lewis and Randall,[1]

$$H_2 + \frac{1}{2} O_2 = H_2O_{(l)}; \quad \Delta F_{298} = -56560 \text{ calories.}$$

hence

$$\Delta F_{298} = 112{,}228 + 2 \times (-56560) - 1365 \log p_{H_2}{}^{*}$$

When $p_{H_2} = 1$ atm., then $\Delta F_{298} = -892$ calories.

Therefore, the driving force of this reaction is

$$E = \frac{892}{2 \times 23074} = 0.0193 \text{ volt.}$$

Even at 25°C. there is a small driving force tending to reduce $Ni(OH)_2$ to Ni, forming water. This accounts for the fact that the spontaneous reduction of nickelous hydroxide takes place under one atmospheric pressure of hydrogen, especially when it is in contact with a catalyst, such as a platinized platinum or nickel.

The free energy change for the reaction,

$$NiO_{(s)} + H_2 = Ni_{(s)} + H_2O_{(l)} \quad \ldots\ldots\ldots (14)$$

may be obtained using the value of the free energy of formation of NiO. The present writer calculated the free energy of formation of NiO from the experimental data of Pease and Cook,[2] and found it to be 49808 calories, while the value reported in Pease and Cook's paper is 56497 calories.

$$Ni_{(s)} + \frac{1}{2} O_2 = NiO_{(s)}; \quad \Delta F_{298} = -49808 \text{ calories.}$$

therefore $\Delta F_{298} = 49808 - 56560 = -6752$ calories.

And the free energy for the reaction

$$Ni^{++} + 2OH^- + H_2 = Ni_{(s)} + 2H_2O_{(l)} \quad \ldots\ldots (15)$$

may be calculated from (7)

$$\Delta F_{298} = -1365 \times 19.557 = -26695 \text{ calories.}$$

Therefore combining reaction (14) and (13), we obtain

$$NiO_{(s)} + H_2O_{(l)} = Ni(OH)_{2(s)}; \quad \Delta F_{298} = -5860 \text{ calories...(16)}$$

(1) Loc. cit.

(2) *J.Am.Chem.Soc.*, **48** (1926), 1196.

* The value of ${}_0p_{H_2}$ which is the critical partial pressure at equilibrium may also be obtained from this equation by putting ΔF equal to zero.

The results above obtained are summarized as follows for the sake of comparison.[1]

$Ni_{(s)} + O_2 + H_2 = Ni(OH)_{2(s)}$; $\Delta F_{298} = -112228$ cals.
$Ni^{++} + 2OH^- + H_2 = Ni_{(s)} + 2H_2O_{(l)}$; $\Delta F_{298} = -26695$ cals,
$NiO_{(s)} + H_2 = Ni_{(s)} + H_2O_{(l)}$; $\Delta F_{298} = -6752$ cals.
$Ni(OH)_{2(s)} + H_2 = Ni_{(s)} + 2H_2O_{(l)}$; $\Delta F_{298} = -892$ cals.
$Ni^{++} + 2OH^- = Ni(OH)_{2(s)}$; $\Delta F_{298} = -25800$ cals.
$Ni^{++} + 2OH^- = NiO_{(s)} + H_2O_{(l)}$; $\Delta F_{298} = -19940$ cals.
$NiO_{(s)} + H_2O_{(l)} = Ni(OH)_{2(s)}$; $\Delta F_{298} = -5860$ cals.

The writer wishes to express his great indebtedness to Professor G. Fuseya for his kind direction.

Summary.

1. The re-activation by the action of the hydrogen of the nickel electrode, which has once been affected by oxygen, has been explained on the ground that nickel itself behaves as a catalyser, on the combination of oxygen and hydrogen.

2. It has been thermodynamically deduced that the equilibrium conditions in the nickel half-cells are expressed by $p_{H_2} \times a_{Ni^{++}} \times a^2_{OH^-} = 10^{-19.56}$, from which it has been calculated that when the activity-product ($a_{Ni^{++}} \times a^2_{OH^-}$) attains the solubility product of nickel hydroxide, the corresponding partial pressure of hydrogen is 0.22 atm. This is the critical pressure above which only equilibrium can be established and if the partial pressure of hydrogen is less than this value the nickel will tend to go into solution accompanied

(1) The writer calculated the solubility product of $Ni(OH)_2$ also from the experimental data of Britton (*J. Chem. Soc.*, **127** (1925), 2114) by the following method and found it to be 2.0927×10^{-17}, while the value reported in Britton's paper is 8.7×10^{-19}. This was done by taking into consideration the decrease in nickel ion concentration resulting from the addition of 0.8 c.c. of 0.0967 N. NaOH to 100 c.c. of 0.025 M. $NiCl_2$ to produce incipient precipitation, by obtaining the activity of Ni^{++} in the solution, taking 0.38 as the activity coefficient at that concentration (Lewis and Randall, "Thermodynamics" p. 382), and combining this activity with the observed value of $a_{OH^-} = 10^{-7.33}$ in the resulting solution.

$$a_{Ni^{++}} = 0.38 \times \left(2.5 \times 10^{-2} - \frac{0.0967 \times 0.8}{2 \times 100}\right) = 0.00935$$

$$a_{OH^-} = 10^{-7.33}$$

hence,

$$a_{Ni^{++}} \times a^2_{OH^-} = 0.00935 \times 10^{-2 \times 7.33} = 2.0927 \times 10^{-17} \text{ or } 10^{-16.68}$$

This value being adopted the values of ${}_0p_{H_2}$ and the free energies of the following reactions become,

${}_0p_{H_2} = 0.0013$ atm.
$Ni(OH)_{2(s)} = Ni^{++} + 2OH^-$; $\Delta F_{298} = 22767$ cals.
$Ni_{(s)} + O_2 + H_2 = Ni(OH)_{2(s)}$; $\Delta F_{298} = -109195$ cals.
$Ni(OH)_{2(s)} + H_2 = Ni_{(s)} + 2H_2O_{(l)}$; $\Delta F_{298} = -3925$ cals.

by the precipitation of nickel hydroxide until p_{H_2} rises to the critical pressure.

3. On the above deduction, the changes with time in the electromotive force of the cells which were prepared in the atmosphere of hydrogen or of nitrogen have been explained.

4. The abnormal behaviour of the nickel electrode observed by previous investigators has also been discussed on the same basis of proof.

5. The changes in free energy of various reactions have been calculated.

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THE PREPARATION OF TRIACETYL STARCH AND ITS MOLECULAR WEIGHT.

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Although it is quite necessary, in the study of starch, to get the solution of starch or of its derivatives, yet our knowledge of this field is far from being complete. The author has given a convenient method of preparing acetyl derivative of starch yielding a large quantity of it at a time, has examined its solubility in various solvents, and has estimated its molecular weight in several media by the cryoscopic and the ebullioscopic methods.

The Acetylation of Starch.

Acetylation of starch has already been carried out in various ways,[1] among which there are fairly available methods such as that with acetic anhydride and pyridine[2] and that with acetic anhydride and sulphuric acid,[3] but still they either take a long time (a few days or more) or are apt to give more or less depolymerised products. It is readily understood that starch cannot be expected to undergo mild acetylation without difficulty in the absence of suitable dispersing medium either for the starch or for the reaction product as in the case of the usual acetylating methods.

(1) See M. Samec, "Kolloidchemie der Stärke," (1927), p. 436.
(2) M. Bergmann and E. Knehe, *Ann.*, **452** (1927), 141.
(3) F. Pregl. *Monatsh.* **22** (1901), 1049; H. Pringsheim and K. Wolfsohn, *Ber.*, **57** (1924), 887.

The author has succeeded in preparing acetyl starch quite easily, overcoming the above difficulty in the following way:

Fourty grams of starch[1] (air-dry, containing 7% of water) are mixed up with a saturated aqueous solution of zinc chloride (50 gr. of anhydrous salt in 23 gr. of water) to a *transparent sticky paste*, heating on the water bath, and 220 c.c. of acetic anhydride are gradually added, a part of which is at first converted by the water into acetic acid, which plays an important rôle as a nice solvent for the acetyl starch which is to be produced. As water often acts with acetic anhydride violently the reaction mixture is carefully warmed (sometimes it must be cooled) with constant stirring on the water bath, the temperature not far exceeding 70°. After the water is acted the gelatinized starch goes into solution quite markedly, the acetylation comes to the end within half an hour. Small lumps of unchanged starch are left, which can no more be attacked on further addition of acetic anhydride. This is centrifuged away and the somewhat turbid, viscous solution, after evaporating off some acetic acid, is poured in ice water. The acetylated product separates out as a flocky precipitate, while zinc chloride and others dissolve in the water. By repeatedly rubbing with fresh water the solid is reduced to a fine powder, which is nearly free from impurity. Yield 60 gr. of the well-dried substance, that is 90% of the theoretical amount.

For the purification the dried acetyl starch was dissolved in hot chloroform and alcohol was added until a turbidity appeared. When allowed to cool, the acetyl starch separated out as a white fine powder, which was filtered and washed with alcohol. Although the pure chloroform solution was left, crystals did not appear, but a thin film like that of collodium was formed on the wall of the vessel.

This acetylated starch is different in several points (temperature of decomposition, solubility, specific rotation, etc.) from any of those already described[2]; when heated in a capillary tube, it sinters at 258° and slowly decomposes over 270°. It dissolves in acetic acid, chloroform (free from alcohol), pyridine, acetic anhydride, conc. sulphuric acid (remaining without a slight decomposition for 20 minutes), ethylene bromide, bromoform, and phenol, far more readily at higher temperatures. The solution is clear when dilute but more or less turbid when over 2–5 percent. It is tolerably

(1) "Starch soluble Merck" is used. It is never "soluble" and swells up with hot water just like the potato starch washed with dilute alkali and dilute acid. The specific rotation (190°) and the content of ash (0.18%) is also the same.

(2) F. Pregl; M. Bergmann and E. Knehe, loc. cit. in which detailed descriptions on its properties, especially on its solubility are deficient.

soluble in acetone, acetic ether, and toluene, less in benzene and carbon tetrachloride, far less in petroleum ether, ether, and alcohols, and almost insoluble in water. In hot toluene it is fairly soluble; a beautiful fluorescence is observed when its solution is allowed to cool.

For the analysis the purified acetyl starch was again dissolved in a mixture of toluene and acetone on the water bath, precipitated with alcohol, and dried at 110° in vacuum over phosphorus pentoxide.

0.1930 gr. of subst. gave 0.3513 gr. CO_2 and 0.0988 gr. H_2O. (Found: C=49.64; H=5.73. $C_6H_7O_5(C_2H_3O)_3$ requires C=49.98; H=5.60%)

The acetyl value was determined by saponifying the substance with a known amount of 1/4 n-NaOH, in warm acetone solution,[1] the excess of alkali being titrated with 1/10 n-HCl, using phenolphthalein as the indicator.

0.1660 and 0.2000 gr. of subst. required 6.93 and 8.37 c.c. of 1/4 n-NaOH respectively. (Found: CH_3CO=44.8; 44.9. $C_6H_7O_5(CH_3CO)_3$ requires CH_3CO=44.8%)

Optical study was made in readily dissolving solvents:

$$[\alpha]_D^{28}=\frac{2.86^\circ\times 100}{1.680\times 1}=170.2^\circ \text{ (in chloroform)},$$

$$[\alpha]_D^{28}=\frac{2.72^\circ\times 100}{1.695\times 1}=160.4^\circ \text{ (in acetic acid)},$$

$$[\alpha]_D^{14}=\frac{2.35^\circ\times 100}{1.471\times 1}=159.6^\circ \text{ (in pyridine)}.$$

The Saponified Product of the Triacetyl Starch. Saponification was carried out most easily in the following way: dried triacetyl starch (2 gr.) was dissolved in hot toluene (40 c.c.) and sodium ethylate (0.6 gr. Na in 15 c.c. C_2H_5OH) was added. Reaction occurred immediately, the vessel being filled with a gelatinous product, which was dissolved on addition of water. The excess of alkali was neutralized with acetic acid. The liquid separated into two layers, namely, a layer of turbid aqueous solution and that of clear toluene, which was separated. The former solution was filtered, evaporated at 40° in vacuum to a small volume (35 c.c.) and poured in methyl alcohol (250 c.c.). The saponified product separated out as a white precipitate, which was filtered and washed with alcohol. It was again dissolved in water and precipitated with alcohol.

(1) In fact, the substance was first dissolved in a small amount of boiling toluene, then acetone (50 c.c.) was added and warmed on the water bath.

It is an amorphous white somewhat hygroscopic powder, forming a clear solution with water when dilute, but an opaque solution when concentrated. It gives a pure indigo-blue colour with iodine and does not reduce Fehling's solution. For analysis it was dried at 110° and 1 mm. over phosphorus pentoxide.

0.2122 gr. of subst. gave 0.3430 gr. CO_2 and 0.1203 gr. H_2O. (Found: C=44.08; H=6.34. $C_6H_{10}O_5$ requires C=44.42; H=6.22%)

$$[\alpha]_D^{21} = \frac{1.98^\circ \times 100}{1.046 \times 1} = 189.3^\circ \text{ (in water).}$$

The original starch used for the acetylation has the specific rotation:

$$[\alpha]_D^{27} = \frac{1.76^\circ \times 100}{0.926 \times 1} = 190.0^\circ \text{ (in water).}$$

Though the saponified product of the acetyl starch is identical with the original starch in the specific rotation and the colouration with iodine, they differ in the following respect: the former dissolves in water, while the latter swells up with hot water, forming the paste.

These two starches cannot, however, be regarded as essentially different, because according to Samec the fraction of starch containing phosphate (amylopectin) forms the paste, while that free from phosphate (amylose) dissolves in water without forming the paste, thus the cause of forming the paste may be attributed to the component containing phosphate[1]; and indeed, when the phosphate is removed, the amylopectin gives a homogenous, not opaque solution[2] and on the other hand, when phosphoric acid is introduced into the amylopectin which is deprived of its phosphate, there is formed a product similar to the original amylopectin.[3] Now, the present saponified product of the triacetyl starch has been found to contain no phosphate, so it is quite natural that it should be more soluble than the original starch containing phosphate. That the soluble saponified product may be essentially "soluble starch" is shown by the fact that its clear solution yields a light cloudy precipitate when left a few days, as is usually the case with the clear solution of amylose.

Finally, it must be mentioned that it was confirmed that during the process of acetylation the starch remains unchanged (in the specific rotation, the colouration with iodine, the behaviour towards water etc.) before the acetyl group is introduced, even under the treatments of gelatinization with zinc chloride solution and heating in acetic acid.

(1) M. Samec and v. Hoefft, *Kolloidchem. Beih.*, **5** (1913), 141.
(2) M. Samec, *Kolloidchem. Beih.*, **6** (1914), 23.
(3) M. Samec and A. Mayer, *Comp. rend.*, **173** (1921), 321.

From these facts it may be said that the starch is not changed (essentially) by the treatments of the acetylation and the saponification.

The Reacetylation of the Saponified Product. Acetyl group was introduced again into the saponified product of the triacetyl starch by the same method, the acetylated product being purified as before. When heated in a capillary tube it sinters at 257° and gradually decomposes over 270°. The specific rotation is also the same as before:

$$[\alpha]_D^{28} = \frac{2.90^\circ \times 100}{1.698 \times 1} = 170.6^\circ \text{ (in chloroform)},$$

$$[\alpha]_D^{28} = \frac{2.86^\circ \times 100}{1.785 \times 1} = 160.2^\circ \text{ (in acetic acid)}.$$

It is concluded, therefore, that the saponified product of the acetyl starch can be brought back to the original acetyl starch by introducing the acetyl group without causing a change.

The Molecular Weight of the Triacetyl Starch.

Since Karrer published an idea that starch may be a polymerised product of a relatively small molecule such as maltose anhydride,[1] other polysaccharides naturally have come to be believed as similarly composed of such small elementary molecules. This idea was directly demonstrated with inulin by the cryoscopic study in liquid ammonia,[2] and with various polysaccharides further direct confirmations of this idea were brought forward also by the cryoscopic investigations of their acetyl derivatives. The conclusions are striking: The triacetyl derivative of cellulose,[3] lichenin[3][8], inulin[4][8], glycogen[5], salep-mannan,[6] amylose[8] in *acetic acid*, and that of amylopectin[8], amylose[7] in *phenol*, all may be considered quite unexpectedly to exist as a single molecule of triacetyl hexosan (mol. wt. 288).

(1) P. Karrer and C. Nägeli, *Helv. Chim. Acta*, **4** (1921), 263; P. Karrer, *Naturw.*, **9** (1921), 399; P. Karrer, *Z. angew. Chem.*, **35** (1922), 85.

(2) L. Schmid and B. Becker, *Ber.*, **58** (1925), 1968; Reichlen and Nestle, *Ber.*, **59** (1926), 1159. From these experiments inulin is considered to exist as such a small molecule as fructose-disaccharide anhydride, but it was recently reported by L. Schmid and G. Bilowitzki (*Monatsch.*, **48** (1927), 163) that no elevation of the boiling point of piperidine is observed upon the addition of inulin.

(3) K. Hess and Schultze, *Ann.*, **448** (1926), 99.

(4) K. Hess and Stahn, *Ann.*, **455** (1927), 104.

(5) K. Hess and Stahn, *Ann.*, **455** (1927), 115.

(6) H. Pringsheim and G. Liss, *Ann.*, **460** (1928), 32.

(7) M. Bergmann and E. Knehe, *Ann.*, **452** (1927), 141.

(8) M. Bergmann, E. Knehe and v. Lippmann, *Ann.*, **458** (1927), 93.

Of these experiments it must, however, be remarked that the depressions of the freezing point giving such a small molecular weight, could be observed only at low concentrations (ca. 0.05—0.5%) and only when observations were carried out not immediately but several hours or several days after dissolving the substance. The investigators explain this phenomenon as due to the disassociation of the large molecule of polysaccharides, which proceeds quite slowly and only in dilute solutions.

Expecting to obtain similar results also in other media which are neutral and indifferent to the substance, the author has made cryoscopic studies of the triacetyl starch in ethylene bromide, bromoform and camphor, and also in acetic acid and phenol, and ebullioscopic studies in chloroform, acetone, and acetic acid. The result is that, in almost all solvents, the depressions of freezing point or the elevations of boiling point were exceedingly small at high or low concentrations. As a comparative study, the author has observed also the freezing point depression of the solvent caused by the acetyl derivative of some simple carbohydrates as glucose and saccharose, the results of which have confirmed that the triacetyl starch exists all the same as a huge, polymerised molecule compared with such simple carbohydrates, even in dilute solutions.

The Cryoscopy. The freezing vessel is so constructed that measurements may be carried out in high vacuum. The stirrer is made of platinum wire, to the top of which a ring of tin-plate is attached, and moved up and down by means of an electro-magnet.(1) The results of the cryoscopic studies of the triacetyl starch using ethylene bromide, bromoform, camphor, and acetic acid as solvent, are given in the following tables.

1. *Ethylene bromide.* Freezing point 9.5°. K=120.(2) It has proved to be an excellent cryoscopic solvent for the acetyl starch, owing to the fairly large dissolving power, the large cryoscopic constant and the ease of purification. It was purified by shaking with a soda solution, drying with calcium chloride, and distilling two times in the space shut off from the moist air. Boiling point 131.2°. After introducing the solvent or the substance, the freezing vessel was evacuated so as to expel the moist air. Evacuation has also the benefit of hastening the dissolving of the substance.

(1) Ostwald-Luther, "Physiko-chemische Messungen," (1925), p. 332.

(2) The mean value of several observers'. See P. Walden, "Molekulargrössen von Elektrolyten in nichtwässerigen Lösungsmitteln," (1923), p. 208.

Triacetyl starch (gr.)	Ethylene bromide (gr.)	Conc. (%)	Depression (degree)	Mol. wt.	Remarks.	
					subst. dissolved at:	observed after: (hour)
0.0148	17.6	0.084	0.004	(2600)		1
0.0148	17.6	0.084	0.003	(3400)		3
0.0305	23.5	0.130	−0.005		60°	3
0.0305	23.5	0.130	0.000			21
0.0266	17.6	0.151	0.004	(4500)	80°	0.5
0.0718	20.8	0.345	0.010	4100	70°	4.5
0.0718	20.8	0.345	0.010	4100		22
0.0748	17.6	0.425	0.010	5100		1
0.1524	17.6	0.865	0.017	6200		3
0.174	19.4	0.897	0.019	5600		20
0.159	17.6	0.903	0.021	5100		1
0.181	19.3	0.938	0.021	5350	60°	6
0.181	19.3	0.938	0.022	5100		26
0.114	17.6	0.648	0.010	8050		0.3
0.463	17.6	2.63	0.051	6400		3
0.463	19.8	2.34	0.057	4900		3.5
0.463	19.8	2.34	0.048	5850		22
β-Pentaacetyl glucose (mol. wt. 390)						
0.151	17.6	0.859	0.251	410		
0.187	17.6	1.062	0.311	410		
0.189	19.8	0.954	0.272	420		
Octaacetyl saccharose (mol. wt. 678)						
0.055	17.6	0.313	0.063	600		
0.073	16.0	0.456	0.085	643		
0.163	17.6	0.926	0.170	652		
0.314	19.8	1.58	0.281	677		
0.489	19.8	2.48	0.422	702		

2. *Bromoform.* Freezing point 7°. K=144.

Triacetyl starch (gr.)	Bromoform (gr.)	Conc. (%)	Depression (degree)	Mol. wt.
0.120	19.4	0.620	0.017	5020
0.144	22.3	0.646	0.020	4650
0.321	22.3	1.44	0.041	5050
β-Pentaacetyl glucose (mol. wt. 390)				
0.148	19.5	0.759	0.276	408
Octaacetyl saccharose (mol. wt. 678)				
0.157	19.4	0.809	0.174	671

3. *Camphor.* Melting point 178°. K=400.

Triacetyl starch (gr.)	Camphor (gr.)	Conc. (%)	Depression (degree)	Mol. wt.
0.1140	0.671	17.0	3.5	1940
0.0674	0.400	16.5	3.1	2120
0.0316	0.553	5.70	1.5	1520

In spite of high concentrations the molecular weight has come out considerably small, about one-third of that found in other solvents. This is probably due to the disassociation of the large molecule caused by the high temperature.

4. *Acetic acid.* Freezing point 16°. K=39. Measurements were carried out in high vacuum, as Hess[1] and Bergmann[2] have recommended in the cryoscopy with the polysaccharide acetate in this solvent, in order to avoid irregular depressions which would occur otherwise.

Triacetyl starch (gr.)	Acetic acid (gr.)	Conc. (%)	Depression (degree)	Mol. wt.	Remarks. observed after: (hour)
0.0110	26.2	0.042	0.007	230	19
0.0110	26.2	0.042	0.010	160	72
0.0400	15.7	0.254	0.120	82	20
0.0400	15.7	0.254	−0.090		72
0.0870	21.0	0.414	0.080	195	21
0.0870	21.0	0.414	−0.050		72
0.0987	22.6	0.436	0.009	1900	1
0.0480	7.40	0.648	0.012	2100	0.5
0.284	24.1	1.13	0.072	610	22
0.284	24.1	1.13	0.008	5600	72
0.100	7.10	1.48	0.030	1910	0.5
β-Pentaacetyl glucose (mol. wt. 390)					
0.0747	7.40	1.09	0.100	393	

It is seen in the table that soon after dissolving the substance, depressions were quite small, then became larger and after more hours became again smaller and in some cases even elevations were observed. The pure

(1) *Ann.*, **448** (1926), 99.
(2) *Ann.*, **458** (1927), 93.

solvent itself being sometimes found to change its freezing point with the time,[1] the author dare not attribute these changes of depression to the dis-association of the acetyl starch or to the reassociation of the elementary molecules thus disassociated.

5. *Phenol.* Freezing point 40°. K=79. Phenol is more difficult to manipulate than acetic acid; the freezing temperature even of pure phenol fell quite irregularly by 0.02° or more at every freezing with all precautions,[2] but no particular depression was observed due to the addition of a small amount (0.3%) of the triacetyl starch.

From the above studies it may be clearly pointed out that such solvents which are not indifferent but sensitive to moisture and air as acetic acid and phenol, quite unlike the neutral solvents, being very liable to cause too large (improper) depressions, are regarded to be no adequate cryoscopic solvent, especially for higher polysaccharides because depressions caused by the addition of them may be considerably small in any case.

The Ebullioscopy. The results of the ebullioscopic studies of the triacetyl starch using acetic acid and chloroform as solvent are given in the following tables. These solvents, being somewhat difficult to manipulate, and elevations of boiling point being quite small, the values of molecular weight are not very reliable, but it is clearly shown that the triacetyl starch has a molecular weight far larger than the (β-pentaacetyl) glucose.

1. *Acetic acid.* Boiling point 118°. K=25.

Triacetyl starch (gr.)	Acetic acid. (cc.)	Conc. (%)	Elevation (degree)	Mol. wt.
0.911	19.5	4.67	0.016	7100
0.911	22.0	4.14	0.017	6100
0.911	23.0	3.96	0.020	5000
β-Pentaacetyl glucose (mol. wt. 390)				
0.690	11.5	6.00	0.330	455
0.690	17.5	3.94	0.240	416
0.690	19.8	3.52	0.241	368

(1) Therefore, in the above determinations the freezing point was also observed of the pure solvent in parallel with the solutions.

(2) Purified phenol with a definite boiling point was frozen in high vacuum.

2. *Chloroform.* Boiling point 61.2°. K=26.

Triacetyl starch (gr.)	Chloroform (cc.)	Conc. (%)	Elevation degree)	Mol. wt.
0.732	17	4.30	0.017	6900
0.732	1	3.48	0.014	6500
0.732		2.93	0.011	6900
0.732	26	2.81	0.013	5600
0.117	10	1.17	0.005	6100

3. *Acetone.* Boiling point 56°. K=22. No measurable elevation of the boiling point was observed on the addition of the triacetyl starch.

The results of the above cryoscopic and ebullioscopic investigations give a conclusion that *the triacetyl starch possesses, at least in some neutral solvents, a molecular weight as large as or more that of 18 times polymerised anhydro-glucose triacetate*[1] $[\{C_6H_7O_5(C_2H_3O)_3\}_{18}=288\times18=5184]$ *and does not seem to be disassociated to the elementary molecules merely by diluting or by leaving the solution,* as other investigators[2] have observed by doing so.

However, in further more dilute solutions the complete disassociation may well take place, but that can no longer be confirmed with the present cryoscopic method.

The author wishes to express his appreciation to Professor T. Soda for his kind advices and inspiring encouragements in the course of this investigation.

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(1) This result is strongly in favour of A. Pictet's estimation that soluble starch (least polymerised) should be tri-hexahexosan (18 times polymerised anhydro-glucose) considering from the specific rotation of some lower polyhexosans. *Helv. Chim. Acta.*, 9 (1926), 33.

(2) K. Hess; M. Bergmann, loc. cit.

KONDENSATION VON PHTALSÄUREANHYDRID MIT *o*-DICHLORBENZOL.

Von **Munenari TANAKA** und **Naozo TANAKA.**

Eingegangen am 10. Oktober 1928. Ausgegeben am 28. November 1928.

Ueber die Kondensation von Phtalsäureanhydrid mit *o*-Chlorphenol ein Zusatz von Borsäure in Schwefelsäure, habe ich schon kurz berichtet. Brauch ich aber Aluminiumchlorid statt Schwefelsäure nach der Vorschrift von Ullmann[1], bekomme ich bei 130° einen schwach gelben Körper, der nach meiner Meinung wahrscheinlich 3′-4′-Oxychlorbenzophenoncarbonsäure[2] ist, die ich aber leider nicht in reinen Zustand habe bringen können. Degegen kann *o*-Dichlorbenzol leicht mit Phtalsäureanhydrid mittelst Aluminiumchlorid kondensiert werden. Hierbei entsteht bei 115° 3′-4′-Dichlorbenzophenoncarbonsäure (2), was ganz genau mit der Arbeit von Sprent[2] übereinstimmt. Steigert man jedoch die Temperatur bis auf 150° so bekommt man wie mit Drück bei 130° 2-3-Dichloranthrachinon.

Bei dieser Gelegenheit möcht ich noch etwas zu meiner letzten Arbeit[3] hinzufügen. Nachdem Herr Mizoshita dieselbe nochmals genau wiederholt hat, fand er folgendes: Er erhitzt *o*-Chlorphenol und Phtalsäureanhydrid mit Borsäure und Schwefelsäure 1 Stunde auf 240° und treibt dann die Temperatur ½ Stunde lang auf 255°, hierbei entstent ein Gemisch von Alizarin und noch etwas unverändertes 1-Oxy-2-chloranthrachinon. Erhitzt er schliesslich 3 Stunden lang auf 255°, so bildet sich Purpurin.

Experimentaler Teil (bearbeitet bei N. Tanaka)

1. **3′-4′-Dichlorbenzophenoncarbonsäure (2).** 15 gr. *o*-Dichlorbenzol, 15 gr. Phtalsäureanhydrid und 30 gr. gepulvertes Aluminiumchlorid werden innig gemischt und erwärmt, hierbei entweicht reichlich Chlorwasserstoff, und die Masse färbt sich bräunlich und wird dickflüssig. Unter Rühren wird dann die Schmelze einige Stunden auf 120° erhitzt. Nach dem Erkalten werden Wasser und verdünnte Salzsäure hinzugefügt und geringe Mengen von unverbrauchtem *o*-Dichlorbenzol mit Dampf abgeblasen. Der

(1) Ullmann, D.R.P. 282493.
(2) Sprent u. Dodd, B.R.P. 204528 (1923). Vergl. Heller u. Schülke, *Ber.*, **41** (1908), 3627.
(3) M. Tanaka, *Proc. Imp. Acad.*, **3** (1927), 82 u. 345; B.R.P. 245584, 256068.

braun gelbe Rückstand wird mit 5 proz. Natronlauge erwärmt. Es scheidet sich die 3′-4′-Dichlorbenzophenoncarbonsäure (2) auf Zusatz von Salzsäure als kristallinisch erstarrende Masse aus. Der aus Benzol mit Tierkohle umkristallisierte Körper zeigt dem Schmelzpunkt 190° und stellt weisse Nadeln dar.

Analyse: 17.30 mg. Subst. gaben 35.80 mg. CO_2 und 3.75 mg. H_2O. (Gefunden: C=56.5; H=2.40. Berechnet für $C_{14}H_8O_3Cl_2$: C=57.0; H=2.71%)

Diese lösen sich gut in heissem Alkohol, Benzol und Eisessig. Erwärmt man die 3′-4′-Dichlorbenzophenoncarbonsäure (2) mit der 10 fachen Menge Schwefelsäure auf dem Wasserbade, so färbt die Lösung bald gelb unter Bildung von 2-3-Dichloranthrachinon, welche bei 265° schmelzen.

2. **2-3-Dichloranthrachinon.** Kondensiert man *o*-Dichlorbenzol mit Phtalsäureanhydrid in Gegenwart von Aluminiumchlorid bei 150° für einige Stunden oder mit Drück bei 130° und arbeitet das Gemisch nach der in oben angegebenen Methode auf, so erhält man gelbe Kristalle. Der aus Eisessig mit Tierkohle umkristallisierte Körper zeigt den Schmelzpunkt 265–267°, gelbe Nadeln bildend.

Analyse: 7.35 mg. Subst. gaben 16.45 mg. CO_2 und 1.20 mg. H_2O (Gefunden: C=61.3; H=1.82. Berechnet für $C_{14}H_6O_2Cl_2$: C=61.7; H=2.17%).

Schmilzt man diese Körper mit Kali, so entsteht Alizarin, was Kirscher[1] schon erwähnte.

3. **1-2-4-Trioxyanthrachinon.** 10 gr. *o*-Chlorphenol, 32 gr. Phtalsäureanhydrid, 20 gr. Borsäure und 160 gr. konz. Schwefelsäure werden auf 255° erhitzt. Die erhaltene Mischung wird, ohne zu kühlen, in kaltes Wasser gegossen, ausgekocht, abfiltriert und getrocknet. Hierauf wird der Farbstoff mit kochendem Toluol extrahiert und daraus umkristallisiert. Aus Eisessig nochmal umkristallisiert, werden rote Nadeln dargestellt. Schmelzpunkt 256°.

Analyse: 13.49 mg. Subst. gaben 32.4 mg. CO_2 und 3.20 mg. H_2O. (Gefunden: C=65.7; H=2.63. Berechnet für $C_{14}H_8O_5$: C=65.7; H=3.13%).

Nov. 1927. Zentrallaboratorium, Dairen.

(1) Kirscher, *Ann.*, **245** (1887), 348; Grandmougin, *Compt. rend.*, **173** (1921), 717; Liebermann, *Ber.*, **35** (1902), 1780.

DEHYDRATE WIRKUNG VON JAPANISCHER SÄUREERDE IN ANTHRACHINONREIHE.

Von **Munenari TANAKA** und **Susumu WATANABE**

Eingegangen am 10. Oktober 1928. Ausgegeben am 28. November 1928.

Ueber die dehydrate Wirkung von Alumina und Silica wurde zuerst von Meilhe[1] und seinen Mitarbeitern in 1918 veröffentlicht und ähnliche Arbeiten sind mit Japanischessäureerde von H. Inoue[2] und K. Ono[3] gemacht worden. Wir haben diese Methode über Anthrachinonderivate angewandt und fanden: Die dehydrate Wirkung von Erde ist nicht so stark wie bei Aluminiumchlorid[4], doch kann Hydrochinon leicht mit Phtalsäureanhydrid mittelst Erde bei 260° kondensiert werden. Brauchen wir aber Brentzkatechin statt Hydrochinon, bekommen wir eine ganz geringe Menge von Hystazarin und Alizarin. Bei Anwendung von Pyrogallol auf diese Weise erhalten wir kein Anthrachinonderivat, sondern Triphenylmethanfarbstoff, nämlich Gallein (bei Aluminiumchlorid resultiert Anthragallol) und schliesslich bekommt man aus α-Naphtol auf diese Weise, α-Oxynaphtacenchinon[5], dagegen nicht aus β-Naphtol.

Bei dem oben angegebenen Beispiel können wir folgendes feststellen: Die Hydroxylgruppe in der *p*-Stelle (oder α-Stelle) hat verwandschaft mit der Carbonylgruppe, d. h. α-Oxyanthrachinon das tautomere *o*-chinoid[6] Form besitzt.

Experimentaler Teil (bearbeitet von S. Watanabe).

1. **Chinizarin** (1-4-Dioxyanthrachinon). Wir erhitzen 20 gr. Phtalsäureanhydrid und 10 gr. Japanische-säureerde (wasserfrei) gut gemischt und treiben die Temperatur auf 350°, 10 gr. Hydrochinon und ein Gemisch von Phtalsäureanhydrid und Erde (10 gr.) wird wechselweise bei 260–270° unter gutem Rühren hinzugefügt. Die Mischung wird nun so lange auf 260° erhitzt, bis eine Probe sich in verdünnter Natronlauge mit violetter

(1) Mailhe und Goden, *Compt. rend.*, **160** (1918), 467 u. 564.
(2) H. Inoue, diese Zeitschr., **1** (1926), 157, 177, 197, 219.
(3) K. Ono, diese Zeitschr., **1** (1926), 248.
(4) D.R.P. 289345.
(5) Deicher u. Weizman, *Ber.*, **36** (1903), 547 u. 719.
(6) M. Tanaka, *Proc. Imp. Acad.*, **3** (1927), 83; C. Graebe, „Chinone", S. 405.

Farbe löst. Nach dem Erkalten wird die Schmelze zerkleinert, mit Wasser gekocht, filtriert und getrocknet. Der Rückstand wird mit siedendem Alcohol extrahiert. Beim Erkalten scheidet sich das Chinizarin als schöne orange Blätterchen aus. Smpt., 194°.

Analyse: 16.40 mg. Subst. gaben 42.10 mg. CO_2 und 4.55 mg. H_2O. (Gefunden: C=69.9; H=3.19. Berechnet für $C_{14}H_8O_4$: C=70.0; H=3.33%).

2. **Hystazarin und Alizarin.** Erhitzt man, wie in Beispiel 1 angegeben, 30 gr. Phtalsäureanhydrid, 10 gr. Brentzkatechin und 20 gr. Erde, so erhält man ein Gemisch von Hystazarin und Alizarin. Beide werden bekannter Weise mit Toluol getrennt. Hystazarin zersetzt bei über 310°. Alizarin Schmilzt bei 289°.

3. **α-Oxynaphtacenchinon.** 20 gr. Phtalsäureanhydrid, 5 gr. α-Naphtol werden mit 10 gr. Erde innig verrieben, das Gemisch unter gutem Rühren schnell bei 250–260° erhitzt, bis eine Probe sich in alkoholischem Kali schön kirschrot löst. Nach dem Erkalten wird die Schmelze pulverisiert und mit siedendem Alkohol extrahiert um unverändertes Rohmaterial zu entfernen. Der Rückstand wird aus Nitrobenzol extrahiert, wobei sich α-Oxynaphtacenchinon als schön gelbe Nadeln, welche bei 303° schmelzen, ausscheidet. Zur Analyse aus Nitrobenzol umkristallisiertes Oxynaphtacenchinon wurde nochmals aus Toluol umkristallisiert und bei 110° getrocknet.

Analyse: 7.01 mg. Subst. gaben 20.10 mg. CO_2 und 2.20 mg. H_2O. (Gefunden: C=78.4; H=3.49. Berechnet für $C_{18}H_{10}O_3$: C=78.8; H=3.65%).

α-Monoxynaphtacenchinon ist in heissem Nitrobenzol oder Toluol leicht löslich, schwerer in Alkohol oder Eisessig. In konzentriertem Alkali ist es unlöslich, in alkoholischem Kali löst es sich schön kirschrot, in Schwefelsäure mit schön karminroter Farbe.

Sept. 24, 1928. Zentrallaboratorium, Dairen.

CRYOSCOPIC STUDIES ON THE TRANSITION POINTS OF THE COMPOUNDS OF ORGANIC SOLVENTS WITH SALTS. I.

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In the ordinary cryoscopy, we observe the univariant behaviour of systems of two components, a solvent and a solute. Similarly any univariant system formed of three or more components is also applicable to this purpose,

and in analogy to the lowering of the freezing point of a single solvent, the lowering of the transition point by the addition of foreign substances was first investigated by Löwenherz[1] in the case of sodium sulphate decahydrate. He found that the transition point of the decahydrate into anhydrous salt, i. e. 32.38°C., was lowered by foreign substances by amount which gave 32.6 as the moleçular depression referred to 100 gr. of the decahydrate. After this investigation similar studies were carried out for salt hydrates by other investigators[2] in succession. Among them Dawson and Jackson state that "the referring of the concentration to 100 gr. of the solution in which the foreign substance is contained is a more convenient and correct procedure." In general, however, if a transition point of a salt hydrate at which it is transformed into an anhydride is to be used, the writer considers it more convenient to prefer the molecular depression referred to 100 gr. of water to that referred to 100 gr. of the molten hydrate or the solution. In the case of sodium sulphate, for example, since 322 gr. of the decahydrate contain 180 gr. of water, the constant referred to 100 gr. of water becomes $32.6 \times \frac{180}{322} = 18.2$, and the experiment may be carried out without using the molten hydrate.

This sort of cryoscopy can be applied also to the systems in which an organic liquid, instead of water, is present as solvent. In case an organic liquid with a strong solvent power has too low a freezing point to be used in the ordinary cryoscopy, this method would be convenient if the solvent combines with some salt to form a compound, of which transition point is in the neighbourhood of room temperatures. In this respect acetone comes in consideration first of all. This excellent solvent has its freezing point at −94.6°C., but forms some acetone compounds with salts, such as $NaI.3CH_3COCH_3$ [trans. pt.=25.5°C.] and $HgCl_2.CH_3COCH_3$ [trans. pt.= 20.7°C.]. At the transition point these compounds are converted into the solid salt and the saturated solution. The results of the cryoscopic measurements carried out with these two systems are given in the following.

It is supposed that salt $[X]$ combines with n molecules of acetone to form acetone compound $[X.nA]$. In Fig. 1 curve (1) represents vapour pressures of the acetone compound dissociating to the salt and acetone vapour, and curve (2) vapour pressures of the system consisting of the salt, the

(1) Löwenherz, *Z. physik. Chem.*, **18** (1895), 70.

(2) Van't Hoff & Dawson, *Z. physik. Chem.*, **22** (1897), 598; Van't Hoff & Müller, *Ber.*, **31** (1898) 2206; Morgan & Benson, *J. Am. Chem. Soc.*, **29** (1907), 1168; Morgan & Owen, ibid., 1439; Dawson & Jackson, *J. Chem. Soc.*, **93** (1908), 344.

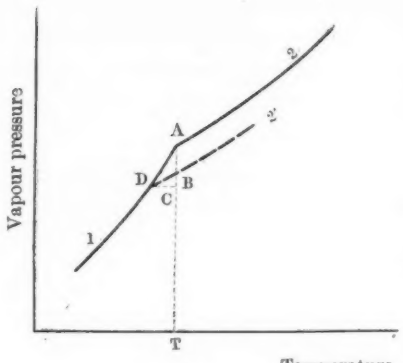

Fig. 1.

solution saturated with respect to the salt and acetone vapour. Curve (2′) shows vapour pressures of the system (2) when another solute is dissolved in it. Here it is assumed that the solute does not appreciably affect the solubility of the salt. A is the transition point, D the lowered transition point, DC the depression of the transition point (ΔT), and AB the depression of vapour pressure (Δp). Applying the Clapeyron-Clausius equation to this case, the following expression is derived for the depression ΔT,

$$\Delta T = \frac{RT^2}{q_1 - q_2} \frac{\Delta p}{p}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where R is the gas constant, T the transition point, q_1 the molar heat of evaporation of acetone from the acetone compound and q_2 the molar heat of evaporation of acetone from the saturated solution. The changes which occur in these two kinds of evaporation may be shown by the following equations.

$$[\mathrm{X}.n\mathrm{A}] = [\mathrm{X}] + n\mathrm{A} - nq_1,$$
$$[\mathrm{X} + c\mathrm{A}] = [\mathrm{X}] + c\mathrm{A} - cq_2.$$

where [] represents a solid phase, ( ) a liquid phase, and a gaseous phase is shown by symbols only. The composition of the liquid phase is given by c, the number of mols of acetone which contains one mol of the salt. From these equations the expression for the melting of the compound is obtained.

$$[\mathrm{X}.n\mathrm{A}] = \frac{c-n}{c}[\mathrm{X}] + \frac{n}{c}(\mathrm{X} + c\mathrm{A}) - n(q_1 - q_2).$$

Now the molar heat of fusion H can be written as

$$H = n(q_1 - q_2). \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

If the concentration of the saturated salt solution and that of the same saturated solution which contains the other solute are given by N and N' in mole fractions, and the corresponding vapour pressures by p and p' respectively,

$$\text{then } \frac{p'}{p} = \frac{N'}{N}, \text{ accordingly } \frac{\Delta p}{p} = \frac{p - p'}{p} = 1 - \frac{N'}{N}.$$

If 100 gr. of acetone contains x gr. of the solute (mol. wt.$=M$),

$$N'=\frac{\frac{100}{58.05}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)+\frac{x}{M}} \quad \text{and} \quad N=\frac{\frac{100}{58.05}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)},$$

where i is the degree of dissociation of the salt in the solution plus unity and 58.05 is the molecular weight of acetone. Here also it is assumed that i and c are not appreciably affected by the existence of the solute. From the above relations follows

$$\frac{\Delta p}{p}=\frac{\frac{x}{M}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)+\frac{x}{M}}, \quad \ldots\ldots (3)$$

where x/M in the denominator may be neglected within the limits of experimental error.

Substituting equations (2) and (3) in equation (1), the following expression for the depression ΔT is obtained.

$$\Delta T=\frac{nRT^2}{H}\cdot\frac{\frac{x}{M}}{\frac{100}{58.05}\left(1+\frac{i}{c}\right)}.$$

If w gr. of the solute is present in W gr. of acetone,

$$\frac{x}{M}=\frac{100}{W}\cdot\frac{w}{M}.$$

Hence

$$\Delta T=\left(\frac{RT^2}{H}\cdot\frac{58.05}{100}\cdot\frac{nc}{(c+i)}\right)\frac{100}{W}\cdot\frac{w}{M}, \quad \ldots\ldots (4)$$

where the term contained in the outer brackets is independent of the nature of the solute and represents the molecular depression K of the transition point referred to 100 gr. of acetone.

Apparatus and Method of Procedure. A Beckmann[1] apparatus with a magnetic stirrer was used for the cryoscopic experiments. The cooling bath was kept constant within 0.1°, and the temperature was such that the convergent temperature was 0.1–0.2° below the transition point. To a known amount of acetone was added a sufficient amount of salt to form the satura-

(1) Beckmann, *Z. physik. Chem.*, **44** (1903), 169.

ted solution and the solid phase, at a temperature one or two degrees above the transition point. The system was then supercooled, a crystal of the new phase, e. g. the acetone compound, was added and the constant maximum temperature was observed. The ordinary procedure of cryoscopy followed, and the molecular depression K was calculated by the expression (4): $\Delta T = K\frac{100\,w}{W\,M}$, introducing the correction for x/M which was eliminated in equation (3).

Preparation of Materials. Acetone was dehydrated by K_2CO_3, and was distilled twice with precaution against moisture.

Sodium iodide was recrystallized from water as $NaI{\cdot}2H_2O$ and was dehydrated by heating. Jones[1] describes that the solution of NaI in acetone was coloured deeply yellow. He supposed at first that this was due to the liberation of iodine but a test with starch paste showed that no free iodine was present, and consequently the yellow colour was ascribed presumably to some reaction between acetone and NaI. According to my experiment, however, the solution was colourless even when saturated and boiled. After some time this turned somewhat yellowish but not deeply yellow.

Mercuric chloride of the Japanese Pharmacopœia was used after drying without further purification.

Other substances were purified by sublimation or recrystallization.

Results. *The case of* $NaI{\cdot}3CH_3COCH_3$. The lowerings of the transition point of this system caused by the addition of each of eight organic compounds were measured, and the results are given in the following table.

TABLE 1.

(1) Solute: Naphthalene (mol. wt. = 128).

Wt. of acetone (W) in gr.	Wt. of NaI in gr.	Wt. of solute (w) in gr.	Observed depression of trans. pt. ΔT	Molecular depression K
23.7	12.0	0.374	0.307	25.1
23.8	11.5	0.769	0.617	24.7
23.7	12.0	0.769	0.642	25.7
23.6	12.7	0.770	0.601	23.9
23.6	12.7	1.408	1.105	24.3
			Mean	24.7

(1) Jones, *Am. Chem. J.*, **27** (1902), 21.

(2) Solute: Camphor (mol. wt. = 152).

W	Wt. of NaI	w	ΔT	K
23.8	11.7	0.585	0.366	22.8
23.7	12.7	0.585	0.369	22.9
23.8	11.7	1.275	0.793	22.8
23.7	12.7	1.275	0.787	22.6
23.8	11.7	1.659	1.025	22.8
				Mean 22.8

(3) Solute: Benzoic acid (mol. wt. = 122).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.432	0.347	23.5
23.8	11.5	0.429	0.349	23.7
23.8	11.5	0.860	0.689	23.6
23.8	11.5	0.862	0.714	24.4
				Mean 23.8

(4) Solute: Acetanilide (mol. wt. = 135).

W	Wt. of NaI	w	ΔT	K
31.5	16.0	0.475	0.273	24.7
23.7	—	0.486	0.358	23.7
23.8	11.5	0.474	0.362	24.7
23.7	11.7	0.485	0.375	25.0
23.7	12.7	0.487	0.380	25.2
23.8	11.5	0.889	0.692	25.4
23.7	12.7	0.892	0.705	25.7
				Mean 24.9

(5) Solute: *p*-Nitranilne (mol. wt. = 138).

W	Wt. of NaI	w	ΔT	K
23.7	—	0.443	0.326	24.2
23.7	12.7	0.443	0.337	25.0
23.7	—	0.586	0.441	24.8
23.7	—	0.737	0.558	25.0
23.7	—	1.332	1.018	25.5
				Mean 25.1

(6) Solute: Phthalic anhydride (mol. wt.=148).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.529	0.346	23.3
23.7	11.5	0.528	0.349	23.4
23.8	11.5	1.055	0.687	23.3
23.7	11.5	1.054	0.691	23.4
			Mean	23.4

(7) Solute: Benzil (mol. wt.=210).

W	Wt. of NaI	w	ΔT	K
23.8	11.5	0.682	0.302	22.3
23.4	11.5	0.665	0.312	23.2
23.7	11.5	0.682	0.323	23.7
23.8	11.5	1.081	0.488	22.8
23.7	12.7	1.081	0.501	23.3
23.4	11.5	1.074	0.509	23.5
23.7	11.5	1.081	0.511	23.8
			Mean	23.3

(8) Solute: Coumarin (mol. wt.=146).

W	Wt. of NaI	w	ΔT	K
31.6	15.0	0.514	0.270	24.4
23.7	11.5	0.508	0.350	24.1
31.6	15.0	1.023	0.533	24.3
23.7	11.5	1.025	0.684	23.5
			Mean	24.1

The mean of these values of the molecular depression is 24.0. The value for each solute differs from the mean at most by amount of 5%, so that this system can practically be used for the cryoscopic measurment.

The values of the transition point obtained in these experiments are given in Table 2, where (I) is the readings of the Beckmann thermometer and (II) is the corresponding temperatures (corrected) in Celcius degree.

TABLE 2.

I	II	I	II	I	II	I	II
3.522	25.48	3.466	25.43	3.500	25.46	3.515	25.48
3.530	25.49	3.498	25.46	3.490	25.45	3.491	25.45
3.501	25.46	3.499	25.46	3.505	25.47	3.499	25.46
3.517	25.48	3.477	25.44	3.501	25.46	3.534	25.50
3.507	25.47	3.493	25.46	3.497	25.46	3.502	25.47
						Mean	25.46

This value is 0.2° lower than 25.7°C. obtained by other authors[1] from the solubility data.

The case of $HgCl_2 \cdot CH_3COCH_3$. Aten[2] gave 13°C. as the transition point of this compound, but according to the measurements similar to the previous case, this point is 20.7°C., 8° higher than the above value as shown in Table 3. Aten's value may be perhaps effected by the insufficiency of the solubility data used in the graphical determination of this point.

TABLE 3.

I	4.818	4.824	4.850	4.789	4.856	4.870
II	20.61	20.64	20.67	20.61	20.68	20.69

The mean : 20.66°C.

In this case if freezing and melting were repeated with the same solution it showed gradual lowering of the transition point, so that this cannot practically be used for the cryoscopic purpose. The acetone solution of $HgCl_2$ was at first colourless, but became yellowish in a few hours, deeply yellow in the next day, and it turned gradually from brown to a brownish black viscous liquid. The molecular depression was determined always using the solutions newly prepared. The results were not so concordant as in the case of sodium iodide. As the mean value of the molecular depression 24 was obtained.

Summary.

1. The lowering of the transition point, at which $NaI \cdot 3CH_3COCH_3$ loses acetone, by the dissolution of foreign substances has been studied and the molecular depression referred to 100 gr. of acetone has been determined

(1) Macy & Thomas, *J. Am. Chem. Soc.*, **48** (1926), 1547. Wadworth & Dawson, *J. Chem. Soc.*, **129** (1926), 2784.

(1) Aten, *Z. physik. Chem.*, **54** (1906), 121.

as 24.0. The transition point has been also determined as 25.5°C. The method may be regarded as the cryoscopy using acetone with an artificially elevated melting point and can be used practically for the molecular weight determination.

2. A similar study has been carried out with $HgCl_2 \cdot CH_3COCH_3$. The molecular depression has been determined as 24 and the transition point as 20.7°C. This system shows, however, some inaccuracy so that it can hardly be applied to the practical cryoscopy.

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